ASSESSMENT OF ION-INDUCED STRATOSPHERIC AEROSOL FORMATION

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By

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Abstract

Based on current knowledge, an assessment of the role of ions
in the stratospheric aerosol formation process is made. From our
order-of-magnitude estimate it is shown that the impact of the
average stratospheric ion population on aerosol formation processed
in the unperturbed stratosphere is not significant.

Introduction

Aerosol can be introduced into the stratosphere (1) by direct transport from the troposphere (including volcanic injection), (2) as a result of downward flux of meteoritic material, or (3) by gas to particle conversion processes occurring in the stratosphere. The most widely accepted explanation for the existence of a sulfate particle layer in the stratosphere ("Junge layer") is that most of the sulfate particles are produced in situ by the oxidation of sulfur dioxide into sulfuric acid vapor which then undergoes either vapor transfer condensation to pre-existing particles or a phase transition to yield new sulfuric acid droplets. It is believed today that gaseous sulfur compounds reach the lower stratosphere by both the continual diffusional transport and by sporadic direct volcanic injections; mainly sulfur dioxide (Junge, 1974). However, Crutzen (1976) recently has suggested that in the absence of violent volcanic activity in-sufficient sulfur dioxide reaches the stratosphere directly from the troposphere to account for the sulfate layer. He has proposed that carbonyl sulfide (CSO) from the troposphere is photolyzed in the stratosphere to produce largely atomic sulfur which then reacts with O_2 to form sulfur dioxide. The principal initiating reaction responsible for the oxidation of sulfur dioxide to eventually sulfuric acid in the stratosphere is thought to be:

$$SO_2 + OH + M \overset{k}{\rightarrow} HSO_3 + M$$

$$\text{with } k = (2 \text{ to } 5) \times 10^{-31} \text{ cm}^6 \cdot \text{sec}^{-1}$$
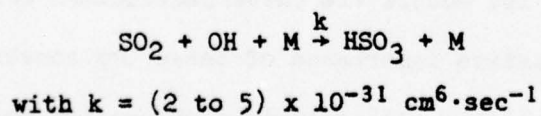
(Davis 1974, Castleman 1974). Other initiating reactions involving $O(^3P)$, $O_2(^1\Delta)$, HO_2, NH_3, CH_3O_2, direct photooxidation, etc., have been

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dismissed since they do not significantly contribute to sulfuric acid formation.

The subsequent steps $HSO_3 \rightarrow H_2SO_4$ have not been identified and established yet and, until proven otherwise, the initiating steps $SO_2 + OH$ is assumed to be rate determining for the formation of sulfuric acid.

The gas to particle conversion process (phase transition) for sulfuric acid can principally be initiated via two main mechanisms:

I. Homogeneous, heteromolecular nucleation

    a) as binary system $H_2SO_4 + H_2O$

    b) as ternary or multicomponent system such as
        $H_2SO_4 + HNO_3 + H_2O$
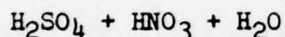
    c) as "ion nucleation"

II. Heterogeneous, heteromolecular nucleation

    a) on the surface of preexisting "sulfate particles"
        (Radius > 0.1μ)

    b) on the surface of preexisting Aitken particles
        (Radius > $50\overset{\circ}{A}$)

    c) on the "surface" of ions - ion growth.

Further growth into the particle size range typically found in the "Junge layer" ($0.1 \lesssim R \lesssim 1\mu$) occurs via (heteromolecular) condensation and coagulation. The relative importance of these two conversion processes cannot be established with certainty at present on the basis of experimental data gathered in the stratosphere or deduced from laboratory experiments.

Various models have been developed focusing on one or several critical physical and/or chemical processes in an attempt to explain features of the stratospheric sulfate layer. For example:

a) One dimensional diffusion models combined with gas phase chemical kinetics but disregarding phase transition processes (Harrison and Larson (1974) and Harker (1975))

b) Homogeneous and heterogeneous nucleation and condensation models combined with limited chemical kinetics but disregarding transport processes (Kiang, et al., (1973), Stauffer, et al., (1973), Yue, et al., (1975), Hofman, et al., (1975)).

Both types of models in turn rely heavily upon stratospheric chemical modelling efforts predicting the concentration of trace constituents such as OH. Furthermore, crucial assumptions have to be made in both models on the physical and chemical state of the atmosphere.

Figure 1 shows the results from diffusion models and their sensitivity to changes of boundary conditions (tropopause height, concentration of sulfur compounds near the tropopause, etc.) and vertical eddy diffusion profiles. Also included in Fig. 1 is the approximate range of stratospheric sulfate measurements as reported by Lazrus and Gandrud (Spring, 1971). Certainly by changing those uncertain atmospheric parameters, the model can be "adjusted" to agree with experimental observations. The models predict steady state maximum sulfate concentrations of 0.08 to 0.27 $\mu g \cdot m^{-3}$ (ambient) or, more accurately, the predictions are for <u>sulfuric acid</u> concentrations of 5.1×10^7 molecules$\cdot cm^{-3}$ (at 18 km), 1.8×10^8 molecules$\cdot cm^{-3}$ (at 12 km), 2.2×10^8 molecules$\cdot cm^{-3}$ (at 12 km) and 1.9×10^8 molecules$\cdot cm^{-3}$ (at 17.5 km).

These sulfuric acid molecules are assumed to be converted immediately into the condensed phase without specifying the conversion process.

Some basic results of model calculations dealing with gas to particle conversion processes are shown in Fig. 3. There are several crucial assumptions in these model calculations which have not yet been fully verified by laboratory measurements. They all influence the rate of formation of new particles. (For example, vapor pressure over binary or ternary solutions, surface tension of embryonic droplets, etc.) However, order of magnitude estimates can be made, and, in conjunction with sensitivity tests, a confidence limit for the accuracy of predictions can be made (Kiang, et al., (1975)). The general conclusion which can be drawn from those model predictions eliminates the "classical" binary phase transition process of $H_2SO_4 + H_2O$ as responsible mechanism for aerosol formation. The critical sulfuric acid concentration required for homogeneous, binary nucleation would be of the order of 3.7×10^8 molecules$\cdot$cm^{-3}. This concentration is higher than the maximum concentration attainable in the stratosphere under steady state conditions as predicted by diffusion models. Under-lying these models is the assumption that the vapor pressure over pure sulfuric acid solution is 10^{-6} Torr, (at 25°C) one of the lowest re-ported in the literature. Conditions for nucleation will be even less favorable for higher vapor pressures. More likely, the H_2SO_4 molecules will condense on preexisting particles as indicated in Fig. 3. Even if the available total surface area per cubic centimeter decreases from 4.5×10^{-8} cm$^2\cdot$cm^{-3} (Castleman, et al., (1975)) to 4.5×10^{-9} cm$^2\cdot$cm^{-3} (corresponding to 0.03 $\mu g\cdot m^{-3}$), homogeneous binary nucleation doesn't

play a dominant role (see Hamill, et al., 1976).

Most likely, however, the gas to particle conversion will occur via ternary nucleation involving H_2SO_4 + HNO_3 + H_2O (Kiang, et al., 1975). This process assumes that $\sim70\%$ H_2SO_4 + $\sim10\%$ HNO_3 + $\sim20\%$ H_2O solution droplets constitute an optimum mixture for which the total vapor pressure is drastically reduced. If the estimated thermodynamic parameters entering the ternary system (vapor pressure and surface tension data) are correct, then this aerosol formation mechanism would be favored against any other process put forth to date. Current information seems to indicate a sufficiently high HNO_3 and H_2O concentration in the stratosphere. The critical concentration of H_2SO_4 required for this ternary nucleation process is less than 10^5 molecules·cm^{-3}. This rather low concentration for aerosol initiation would warrant a constant source for stratospheric particles. This H_2SO_4 concentration is also by at least one order of magnitude lower than required by Hofman, et al. (1975) for their proposed heterogeneous condensation model. Their model involves Aitken nuclei diffusing from the troposphere into the stratosphere and encountering a gaseous sulfuric acid layer (10^6 H_2SO_4 molecules·cm^{-3} max) between 16-22 km altitude. Condensation of H_2SO_4 on those Aitken particles then leads to particle sizes and concentration profiles as found in the "Junge layer".

Some of the pre-existing stratospheric aerosol originates from extraterrestrial sources. Newkirk and Eddy (1964) have estimated the relative concentration of meteoritic debris in aerosols (at 20 km) and concluded that, over a size range of 0.1 to 2μ radius, it represents less than 10 per cent. A completely "particle free" (R > 0.1μ) stratosphere

is therefore an unreasonable assumption.

It has become obvious that most of our understanding of stratospheric aerosol formation leans heavily on model predictions. Models have not yet been fully validated for the stratosphere and hence contain physical and/or chemical parameters that might be quite different from reality.

The above attempt to summarize the current opinions on stratospheric aerosol formation processes constitutes a necessary prerequisite for critically assessing the role of ions in this important aspect of stratospheric chemistry. The understanding of stratospheric ion chemistry is incomplete, mostly derived from laboratory experiments and ionospheric research work, but not yet validated by stratospheric in situ measurements. It is within this framework of uncertainty that the role of ions in stratospheric chemistry (aerosol formation) is being discussed and compared—on a competitive basis—with homogeneous and and heterogeneous reactions of the electrically neutral atmosphere.

Ions

The formation and nature of ions of atmospheric importance has been summarized by Mohnen (1971, 1974) and Ferguson (1975). The evolution and final composition of atmospheric ions strongly depends upon their collisional interaction with the neutral atmosphere and thus becomes a function of altitude (and temperature). The equilibrium concentration of ions is governed by a budget equation:

$$\frac{dn}{dt}^{(+ \text{ or } -)} = q - \alpha n^+ \cdot n^- - n^{(+ \text{ or } -)} \cdot \int_{R_{min}}^{R_{max}} \beta(R) \cdot f(R) dR \qquad (1)$$

$n^{(+ \text{ or } -)}$:   ion concentration

q: ion formation rate

α: recombination coefficient for positive and negative ions

$\beta(R)$:   ion annihilation coefficient with atmospheric aerosol

$f(R)$:   aerosol size distribution function

R: radius of aerosol particles

Zikmunda and Mohnen (1972) have evaluated the integral $\int_{R_{min}}^{R_{max}} \beta(R) \cdot f(R) dR$ for the stratosphere and found it to be much smaller than the ion loss due to recombination for the unperturbed stratospheric particle load. The ion formation rate q, derived from cosmic radiation, is shown in Fig. 4.

Typical values between 20 and 50 ion pairs$\cdot$cm$^{-3}\cdot$sec^{-1} can be expected within the altitude range of 10-20 km, with a maximum around 12 km. The recombination coefficient is of the order of 1×10^{6} cm$^{3}\cdot$sec^{-1} which leads to <u>average</u> ion equilibrium concentrations ($n = \left(\frac{q}{\alpha}\right)^{-\frac{1}{2}}$) of
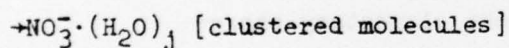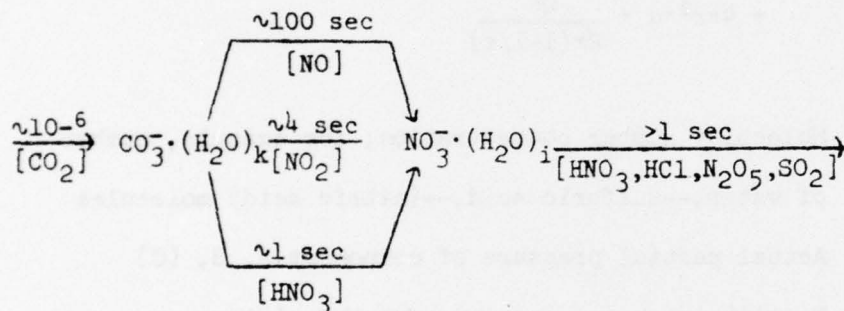
$$4400 < \left(\frac{q}{\alpha}\right)^{-\frac{1}{2}} < 7000 \text{ ions} \cdot \text{cm}^{-3}$$

Actual measurements in the stratosphere (summarized by Hake (1973)) reveal ion profiles that follow the ionization profile and fall within the concentration range of 1000 - max 10,000 ions$\cdot$cm^{-3}. For our purpose of ion assessment, we will assume two ion concentration values: $n = 1000$ cm^{-3} and $n = 5000$ cm^{-3} and thus cover minimum and average conditions. The average lifetime (e^{-1} value) of ions in the stratosphere thus becomes 1000 sec and 200 sec, respectively. As mentioned earlier, the chemical composition of ions depends upon the gas composition and the "reactivity" of these molecules with particular ion species. The

average stratospheric concentration profiles for gases, particles (large particles and condensation nuclei or "Aitken particles") and ions are illustrated in Fig. 5. Ions can conceivable alter their chemical nature as they collide with neutral gas molecules. From this emerges the concept of "initial ions → intermediate ions → terminal ions." The boundary conditions of a limited average lifetime for ions determines the minimum concentration level for which ion-molecule interactions can occur. Assuming an ion-molecule reaction rate constant of 5×10^{-10} $cm^3 \cdot sec^{-1}$ fixes this lowest trace gas concentration to 3×10^6 $molecules \cdot cm^{-3}$ (for 1000 sec average ion lifetime) as indicated in Fig. 5. For a more detailed consideration, measured reaction rate constants for a specific ion molecule process should be used. Those rate constants available to date have been compiled by Ferguson (1975).

Our current understanding of the nature of positive ions at 20 km altitude as derived from measured reaction rate constants and measured and/or estimated stratospheric molecular concentrations (Table 1) is that the terminal ion is predominantly of the type $H_3O^+ \cdot (H_2O)_n$ with $n = 4$ ($\approx 0.4\%$), $n = 5$ ($\approx 35\%$), $n = 6$ ($\approx 60.6\%$) and $n = 7$ (4%). One can expect, due to the high collision frequency, that nitrogen molecules are also clustered to these terminal ions. One of the unresolved problems in stratospheric ion chemistry relates to the amount of gaseous ammonia present in the stratosphere since it reacts via proton transfer with the hydronium ion to form mixed clusters of the type $NH_4^+(NH_3)_m \cdot (H_2O)_n$ (this type of ion constitutes the predominant terminal ion core in the lower troposphere). If the ammonia concentration in the stratosphere is below 3×10^6, then no collisional interaction occurs on the average.

For negative ions, the transition from initial ions to terminal ions is considerably more complicated than for positive ions and involves most every molecular specie listed in Fig. 5. The simplified ion evolution sequence valid in the stratosphere is currently thought to be (Ferguson (1975)):

$$\text{Electron} \rightarrow O_2^- \xrightarrow[\text{$\sim 10^{-5}$ sec}]{[O_2]} O_4^- \dashrightarrow O_2^- \cdot (H_2O)_n \xrightarrow[[O_3]]{\sim 10^{-3} \text{ sec}} O_3^- \cdot (H_2O)_m \rightarrow$$

$$\xrightarrow[[CO_2]]{4 \times 10^{-6} \text{ sec}} CO_4^- \cdot (H_2O)_{1,2}$$

$$\xrightarrow[[CO_2]]{\sim 10^{-6}} CO_3^- \cdot (H_2O)_k \underset{\begin{array}{c}\frac{\sim 100 \text{ sec}}{[NO]} \\ \frac{\sim 4 \text{ sec}}{[NO_2]} \\ \frac{\sim 1 \text{ sec}}{[HNO_3]}\end{array}}{} NO_3^- \cdot (H_2O)_i \xrightarrow[[HNO_3, HCl, N_2O_5, SO_2]]{>1 \text{ sec}}$$

$$\rightarrow NO_3^- \cdot (H_2O)_j \text{ [clustered molecules]}$$
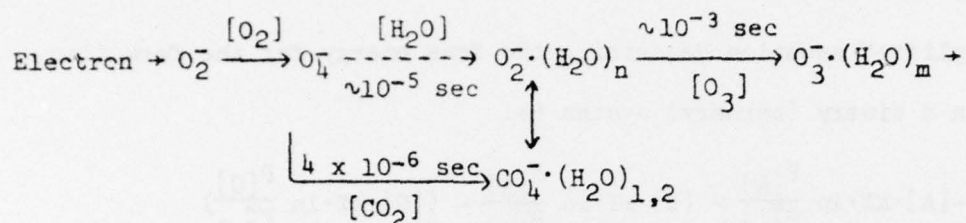
Ion Nucleation

Ion induced nucleation is a well established laboratory phenomena in atmospheric sciences although it does not play any major role in cloud physics in the lower part of the troposphere. Ion nucleation occurs principally at a supersaturation ratio lower than is required for homogeneous nucleation because of the reduction in the free energy barrier.

In the stratosphere, ion nucleation can only occur via heteromolecular nucleation, i.e., involving two or more gaseous components such as $H_2SO_4+H_2O$ or $H_2SO_4+HNO_3+H_2O$, etc., since the supersaturation ratio normally never reaches or exceeds 3.8, the required value for a <u>pure</u> water system.

The simplified equation describing the free energy for the formation of embryos in a binary (ternary) system is:

$$\Delta G = -[A] \cdot kT \cdot \ln \frac{P_{[A]}}{P_{[A]}^{\infty}} - [B] \cdot kT \cdot \ln \frac{P_{[B]}}{P_{[B]}^{\infty}} - ([C] \cdot kT \cdot \ln \frac{P_{[C]}}{P_{[C]}^{\infty}})$$

$$+ 4\pi r^2 \cdot \alpha + \frac{Q^2}{2r(1-1/\epsilon)}$$

(2)

$[A]$, $[B]$, $([C])$:	Molecular number concentration; for example, number of water,--sulfuric acid,--(nitric acid) molecules
$P_{[A]}$, $P_{[B]}$, $(P_{[C]})$:	Actual partial pressure of component A, B, (C)
$P_{[A]}^{\infty}$, $P_{[B]}^{\infty}$, $(P_{[C]}^{\infty})$:	Equilibrium vapor pressure for the <u>mixture</u>
Q:	Ion charge, normally one elementary charge
r:	Cluster radius
ϵ:	Dielectric constant

A general solution of this ion-induced heteromolecular nucleation process as a function of relative humidity is not available to date. However, Castleman and Tang (1972) have extensively studied ion nucleation in a pure water system (unimolecular) and some of their general conclusions can be applied here: The steady state concentrations of ion clusters do not increase continuously from the small hydrates up to and including the critical (stable) embryo as the supersaturation ratio

increases. The existence of a continuously increasing concentration is not a prerequisite to their participation in the nucleation process. Conceivably, the free energy barrier for nucleation can be different for different ion species irrespective of their sign (positive or negative). The structure and bonding of the small ion clusters are the physical and chemical factors leading to the macroscopically observable different values of supersaturation ratios required for different ions. It becomes obvious from the work of Castleman and Tang that a single term, $Q/r \cdot (1-1/\epsilon)$ cannot adequately describe binary or ternary ion nucleation systems, and is at the most suitable for obtaining order of magnitude estimates.

Keeping these constraints in mind, Wiendl (1974) has estimated the ΔG values (from equation 2) for the clustering of $H_2SO_4-H_2O$ around ions. The important conclusion that can be derived from this study is that these cluster ions (as found by Castleman (1974) in the pure water system) do not increase continuously up to and including the stable embryo. One can also deduce from Wiendl's results that under stratospheric conditions, the number of H_2SO_4 molecules clustered to the (positive or negative) ions must be less than three: Wiendl calculated the $H_2SO_4-H_2O$ ion cluster distribution for $25°C$, relative humidity 50%, $P_{total} = 760$ Torr, $P_{H_2SO_4} = 10^{-11}$ Torr (actual partial pressure, the saturation vapor pressure over pure H_2SO_4 solution was assumed to be 10^{-6} Torr) and found the most probable ion cluster to contain two H_2SO_4 molecules with 4–12 water molecules attached (peaking at $n_{H_2O} = 9$).

Kiang and Stauffer (1973) (see also Hamill, et al., 1976) have obtained order of magnitude estimates for ion induced nucleation rates (based on equation (2)) in the binary $H_2SO_4-H_2O$ system and found the minimum H_2SO_4 concentration required for ion nucleation to be by a factor of ten lower than without ions, i.e., under stratospheric conditions of the order of 3×10^7 molecules$\cdot cm^{-3}$ (at 1% relative humidity, decreasing with increasing rh (See text to Fig. 3)). When calculating the characteristic time for ion-induced binary nucleation, one must keep in mind that it depends on the number of ions available. Once the H_2SO_4 concentration required for ion nucleation is reached, all ions will simultaneously become "stable embryos" and grow into larger particles. Therefore the total number of stable embryos is limited to the number of ions present. The size of these critical embryos is in the range of 4 to 8Å. Assuming $r_{embryo} = 5$Å leads to a specific surface area of $A = 3 \times 10^{-11}$ $cm^2 \cdot cm^{-3}$ for 1000 ions$\cdot cm^{-3}$ and 1.5×10^{-10} $cm^2 \cdot cm^{-3}$ for 5000 ions$\cdot cm^{-3}$. This yields (see text to Fig. 3) for 1000 ions$\cdot cm^{-3}$

$$\rightarrow \tau_{ion} = \left(\frac{k \cdot T}{2 \cdot \pi \cdot m_{H_2SO_4}} \right)^{-\frac{1}{2}} \times A^{-1} = 6 \times 10^6 \text{ sec}$$

and for 5000 ions$\cdot cm^{-3}$

$$\rightarrow \tau_{ion} = 1.2 \times 10^6 \text{ sec. (See Fig. 3)}$$

The influence of relative humidity dependence on τ_{ion} enters through the size of the critical (stable) ion embryo but changes between $1 < rh < 10$% are not expected to cause more than one order of magnitude change. Comparing these characteristic times for ion-induced nucleation

with the characteristic time for the H_2SO_4-H_2O ion-free system (Fig. 3) forces us to the conclusion that ion-induced nucleation does not play a dominant role in stratospheric nucleation. Except for very low humidities, it constitutes the least likely mechanism and yields orders of magnitude higher characteristic times than the condensation process on preexisting particles. If, under perturbed stratospheric conditions, the ion density locally and/or regionally increases by more than one order of magnitude, then ions could compete with the homogeneous binary nucleation. But in order to become the dominant phase transition mechanism, one would have to additionally postulate a very low atmospheric total particle load (less than 10^{-9} $cm^2 \cdot cm^{-3}$).

Whether or not the postulated ternary nucleation process involving H_2SO_4 ($\sim$70%) - HNO_3 ($\sim$10%) - H_2O ($\sim$20%) exists is still uncertain. Unlike the case for the H_2SO_4-H_2O system, there exist to date no experimental data--either laboratory simulation experiments or thermodynamic data on vapor pressures--on this ternary system. However, as far as ion involvement is concerned, this unresolved problem has little consequence on the conclusions made so far on ion-induced nucleation:

1) The minimum H_2SO_4 concentration required for the ternary nucleation is of the order of $10^5 \cdot cm^{-3}$ under stratospheric conditions. During the average lifetime of an ion (200-1000 sec), it would not collide with any H_2SO_4 molecules, and, therefore, ion nucleation in the stratosphere would have to be treated as a unimolecular process involving H_2O only and requiring supersaturation ratios (with respect to water) in excess of 3.8. In principle, one must postulate for any ion-induced nucleation process involving one or more molecular species (of low volatility)

in <u>addition</u> to water that the molecular species is (are) clustered to
the ion. This requires a minimum concentration of at least
3×10^6 molecules·cm^{-3}. Should the stratospheric concentration of
H_2SO_4 be below this level (as it would be if the ternary H_2SO_4 (70%) –
HNO_3 (10%) – H_2O (20%) system exists, since the equilibrium vapor
pressure over a mixed solution droplet of this composition is
$<10^{-6}$ Torr), then ion-induced nucleation would not occur at all.

2) The boundary condition for ion nucleation is that there can
only be as many stable embryos formed as there are ions present. This
automatically establishes and <u>limits</u> the characteristic time τ_{ion}
around $>10^6$ seconds for ion densities normally present in the <u>un</u>-
perturbed stratosphere.

Ion Growth

The existence of ion growth is an experimentally well documented
fact in the lower part of the troposphere. Electrical mobility
measurements of small ions seem to correlate well with the "age" of
ions; a longer interaction time with the neutral gaseous environment
yields lower mobility values. This phenomena is, of course, easily
explainable with the concept of ion evolution (Fig. 5), i.e., collisional
interaction with various trace gases of lower and lower concentration
as the lifetime of ion increases (Mohnen (1974)). Typical mobility
measurements in the lower troposphere reveal a broad, continuous
"spectrum" peaking around 1.2 $cm^2 \cdot v^{-1} \cdot s^{-1}$. The initial ion mobility is
usually in excess of 2 $cm^2 \cdot s^{-1} \cdot v^{-1}$. While ion mobility measurements do
not uniquely relate to the mass of ions, they nevertheless are a good

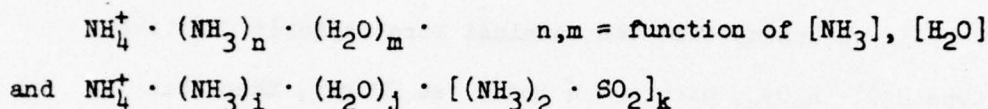indicator for obtaining some information on the average ion mass. Fig. 6 shows these ion mobility measurements for the stratosphere, ranging from 0.5 to 1.5 $cm^2 \cdot v^{-1} \cdot s^{-1}$ at 20 km. Whether or not this spread is real or exhibits artifacts of individual instruments is subject to some debate. There are only a very few mobility data available from the stratosphere. If we assume that the terminal stratospheric positive ion is of the type $H_3O^+ \cdot (H_2O)_n$, with n = 6 and 7 (at 20 km), then this would yield a single mobility value of around 1.75 $cm^2 \cdot v^{-1} \cdot s^{-1}$ for S.T.P. (Mohnen (1974)).

A departure towards lower values would be indicative of molecules clustered to this core ion. The most likely candidate is, of course, N_2. (Although its clustering ability is very low, the high collision frequency would still allow for some attachment.) We are again forced to retreat in the area of simple model calculations based on laboratory measurements in an attempt to assess the existence and importance of ion growth in the stratosphere. To date there have been two mechanisms observed by which ions can grow:

1) The usual ion molecule cluster development whereby the cluster size and the nature of clustered molecules reflect and are in a pseudo equilibrium with the surrounding gaseous environment. The forces by which every molecule is held together within the cluster are hydrogen bonding and/or electrostatic. Their growth is limited by the free energy barrier for nucleation.

2) Chemical reactions that occur between clustered molecules, or chemical reactions between ion clusters and impinging gas molecules whereby the reactant product is incorporated within the ion cluster. There is

virtually no information available on this type of ion chemistry except Kadlecek's laboratory experiments where ion growth was established in a system containing air and variable amounts of water vapor, ammonia and sulfur dioxide. The ions that were mass identified and mobility analyzed were in general

$$NH_4^+ \cdot (NH_3)_n \cdot (H_2O)_m \cdot \qquad n,m = \text{function of } [NH_3], [H_2O]$$

and $NH_4^+ \cdot (NH_3)_i \cdot (H_2O)_j \cdot [(NH_3)_2 \cdot SO_2]_k$

Individual mobility peaks were observed, ranging from

2.46 $cm^2 \cdot v^{-1} \cdot s^{-1}$ (for $NH_4^+ \cdot (NH_3)_{2,3}$) down to

1.17 $cm^2 \cdot v^{-1} \cdot s^{-1}$ (for $NH_4^+ \cdot (NH_3)_{3,4}) \cdot [(NH_3)_2 \cdot SO_2]_4$ and lower.

At the same time, some evidence of particle formation of size $\gtrsim 25\overset{\circ}{A}$ radius was obtained, the total number of particles being, however, by at least two orders of magnitude lower than the ion concentration. For these types of ion molecule reactions, there appears to exist no energy barrier to cluster growth. As these "crystal-like structured" clusters develop, the addition of more mass enhances the stability of the cluster (Castleman (1973)). McLaren, et al., (1973) have determined reaction enthalpies for $(NH_3)_2 \cdot SO_2$ of -45 Kcal·mole^{-1} and -34 Kcal·mole^{-1} in the presence and absence of water vapor.

In a system containing air, ammonia and hydrochloric acid, Mohnen and Coffey (1972) have found particles to be produced at ammonia concentrations as low as 100 parts per trillion. In the absence of ions, particle formation ceased. They postulated an overall ion reaction scheme $NH_4^+ \cdot (NH_3)_i \cdot (H_2O)_j + n \cdot HCl \rightarrow$ particles as being responsible for the described phenomena. Fehsenfeld (personal communication, 1975) has found, however, that the postulated ion molecule reaction is endothermic

at least for all i<3 and j<2. The exact mechanism of this ion-induced
aerosol formation process is therefore not known at this time. Growth
processes involving negative ions and leading to particle formation have
not been reported to date, which does, however, not exclude their existence.
There are conceivably other atmospheric trace gases, particularly reactive
hydrocarbons, ozone and oxides of nitrogen, that could undergo a chemical
transformation after attachment to the ion cluster and cause it to
grow slowly into a larger and more stable complex. The conditions are
favorable for such processes in the lower part of the troposphere. (Most
of the trace gases mentioned above are present in concentrations ex-
ceeding 10^{10} molecules·cm^{-3} and hence allow for at least 10^3 collisional
interactions during the average lifetime of ions.) But not even there
does the average ion grow beyond a mass corresponding to ~1.2 $cm^2 \cdot v^{-1} \cdot s^{-1}$.
Ions having a mobility lower than 0.5 $cm^2 \cdot v^{-1} sec^{-1}$ constitute less than
5% of the total ion population.

In the stratosphere the concentration levels of trace gases such as
NH_3, SO_2, reactive hydrocarbons, etc., are considerably lower. As mentioned
above in the section on "Ions," the average positive and negative ion
will not collisionally interact with any molecular constituents having a
concentration less than 3×10^6 molecules·cm^{-3}. Although the NH_3 concen-
trations in the stratosphere have not been measured yet, current estimates
from various investigators (Crutzen, personal communication, 1975) tend
to be values less than 5×10^7 molecules·cm^{-3} (20 km). If this is the
case, then ion growth due to the $(NH_3)_2 \cdot SO_2$ complex (the only mass
spectrometrically identified ion growth process reported to date) is
very unlikely to occur in the stratosphere since it requires first the

formation of $NH_4^+ (NH_3)_n$ core ions. This is only achievable if $[NH_3] > 10^9$ molecules$\cdot cm^{-3}$. For the same reason, one can exclude the ion-induced NH_3-HCl particle formation reaction. Any chemical reaction between OH and ions is also unlikely to occur. (See Table 1 and Fig. 5 for the concentration range of OH.)

One can conclude that ion growth leading to larger, more complex and stable ions, and eventually to particle formation, is not favored in the unperturbed stratosphere.

Even if there were yet undiscovered chemical reaction mechanisms by which ions could grow into particles that are stable after the recombination process, then their final fate would be coagulation with preexisting particles rather than condensational growth into large "sulfate particles":

$$\tau_{coagulation} = \frac{1}{K_{1,2} \cdot N_1}$$

$K_{1,2}$: coagulation coefficient $\overset{\sim}{} 10^{-6}$ cm$^3\cdot$sec^{-1} for $R_2 \overset{\sim}{} 5\overset{o}{A}$

N_1: preexisting particles ≥ 1 cm^{-3} for $R_1 \geq 0.1\mu$

$\tau_{coagulation}$: $\overset{<}{\sim} 10^6$ sec

This characteristic time has to be compared with the characteristic time for condensational growth.

$$\tau_c = \left(\frac{k \cdot T}{2 \cdot \pi \cdot m_{H_2SO_4}}\right)^{-\frac{1}{2}} \times A^{-1} = 2.3 \times 10^8 \text{ sec}$$

for $A = 2.5 \times 10^{-13}$ cm$^2\cdot$cm^{-3} ($5\overset{o}{A}$ Radius and 100 Particles$\cdot$cm^{-3}). We assume here that only a fraction of the total ion population can grow into stable particles (100 cm^{-3}). Ion growth mechanisms can therefore not be responsible for the formation of the "Junge layer."

Conclusion

This ion assessment with respect to aerosol formation in the stratosphere is based on numerous assumptions, model predictions, deductions from processes occurring in other parts of the atmosphere, and last but not least, on rough order of magnitude estimates. With those limitations in mind, one may conclude that the impact of the average stratospheric ion population on aerosol formation processes in the unperturbed stratosphere is not significant.

In order to have a better understanding of the role of ions in the stratospheric aerosol formation processes, in situ measurements of concentrations of ions, OH, SO_2, NH_3 and aerosol size and number distribution must be made. Also, laboratory investigation and theoretical study on the thermodynamic and kinetic properties of the formation of ion cluster involving multi-component system are needed.

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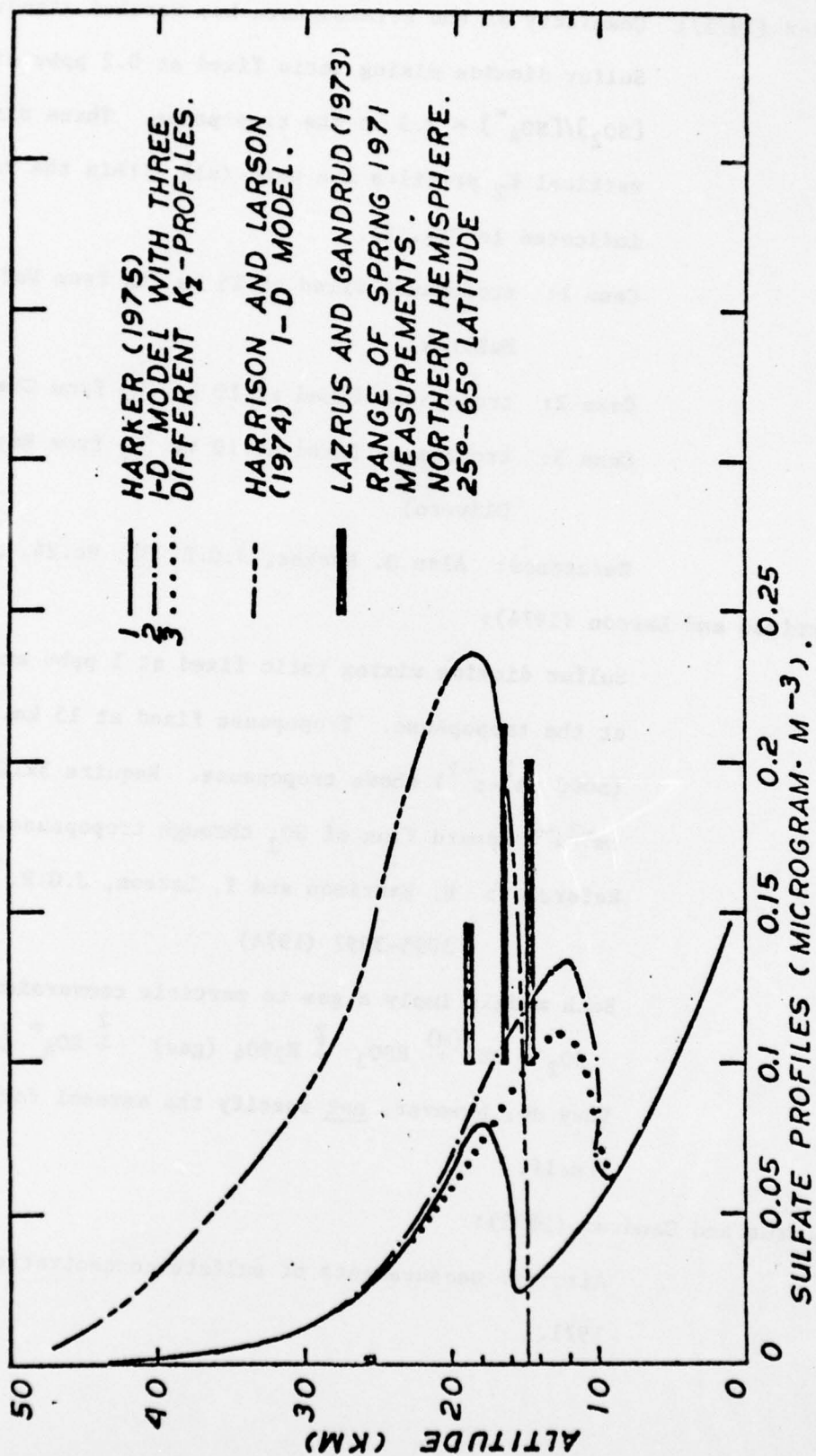
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Figure 1

STRATOSPHERIC SULFATE PROFILES

1. HARKER (1975)
   1-D MODEL WITH THREE
   DIFFERENT K_z-PROFILES.

HARRISON AND LARSON
(1974) 1-D MODEL.

LAZRUS AND GANDRUD (1973)
RANGE OF SPRING 1971
MEASUREMENTS.
NORTHERN HEMISPHERE.
25°- 65° LATITUDE

SULFATE PROFILES (MICROGRAM·M^{-3}).

References

Fig. 1.

Harker (1975): Chemistry of the stratosphere has reached steady state. Sulfur dioxide mixing ratio fixed at 0.2 ppbv and $[SO_2]/[SO_4^-] = 3.3$ at the tropopause. Three different vertical K_Z profiles are used (all within the range as indicated in Fig. 2).

    Case 1: tropopause fixed at 15 km (K_Z from Wofsy and McElroy)

    Case 2: tropopause fixed at 10 km (K_Z from Chang)

   Case 3: tropopause fixed at 10 km (K_Z from Hays and Olivero)

    Reference: Alan B. Harker, J.G.R. 80, No.24, 3399-3401 (1975)

Harrison and Larson (1974):

Sulfur dioxide mixing ratio fixed at 1 ppbv and $[SO_4^-] = 0$ at the tropopause. Tropopause fixed at 15 km. K_Z constant ($5000 \ cm^2 \cdot s^{-1}$) above tropopause. Require 3×10^8 molecules$\cdot$ $cm^{-2}s^{-1}$ upward flux of SO_2 through tropopause.

Reference: H. Harrison and T. Larson, J.G.R. 79, No.21, 3095-3097 (1974)

Both models imply a gas to particle conversion process:

$$SO_2 + OH \overset{(M)}{\to} HSO_3 \overset{2}{\to} H_2SO_4 \ (gas) \overset{2}{\to} SO_4^- \ (aerosol)$$
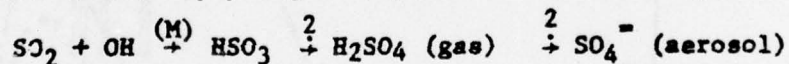
They do, however, not specify the aerosol formation process itself.

Lazrus and Gandrud (1973):

Aircraft measurements of sulfate concentrations for Spring 1971.

Cont'd Fig. 1

Bars indicate the approximate range of SO_4^- at altitude

15, 17, and 19 km. (25°–65° latitude.)

Reference: A.L. Lazrus and B.W. Gandrud, "Progress report

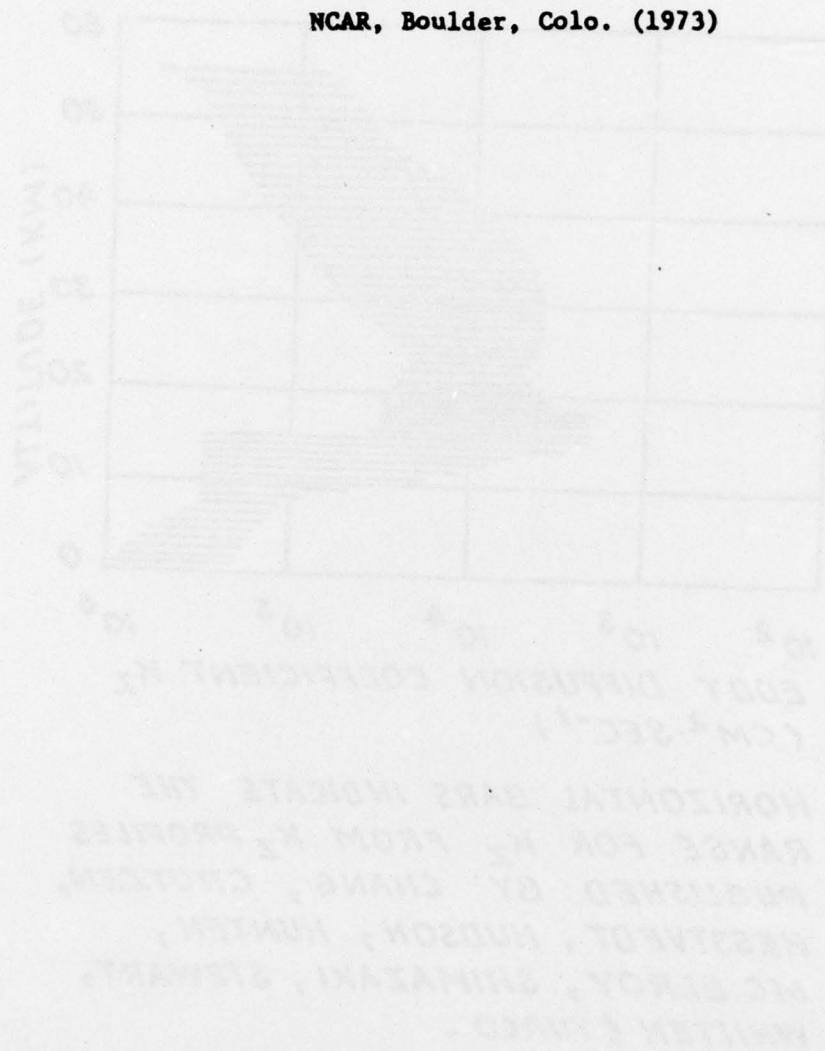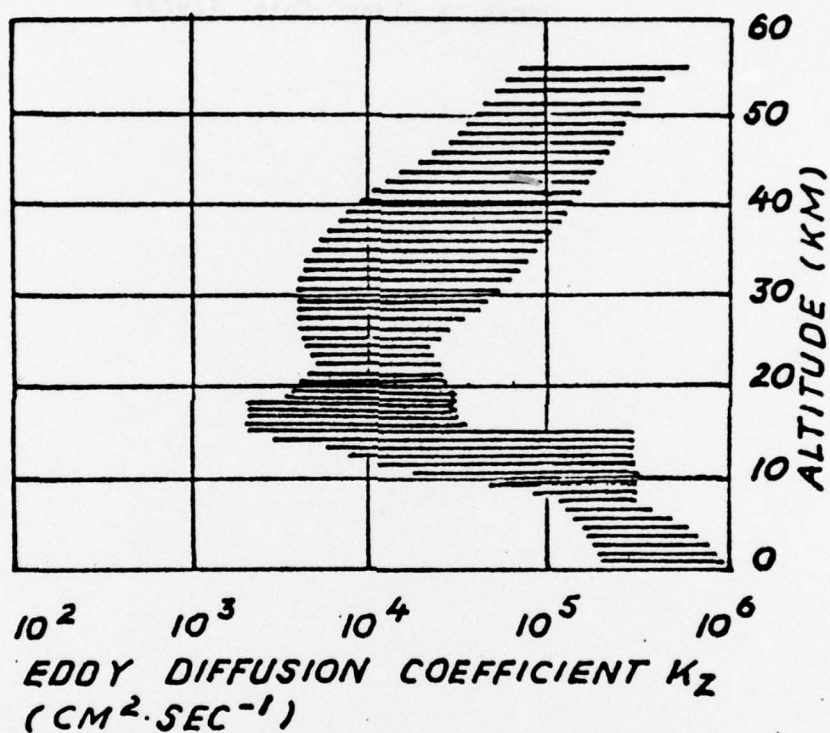on systematic study of stratospheric aerosol."

NCAR, Boulder, Colo. (1973)

Figure 2

EDDY DIFFUSION COEFFICIENT K_Z
$(CM^2 \cdot SEC^{-1})$

HORIZONTAL BARS INDICATE THE
RANGE FOR K_Z FROM K_Z PROFILES
PUBLISHED BY CHANG, CRUTZEN,
HESSTVEDT, HUDSON, HUNTEN,
MC ELROY, SHIMAZAKI, STEWART,
WHITTEN & TURCO.

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Fig. 2.

J. Chang: Proceedings of the Third CIAP Conference. Doc. No. DOT-TSC-OST-74-15 (1974)

P.J. Crutzen: Can.J.Chem., 1569-1581 (1974)

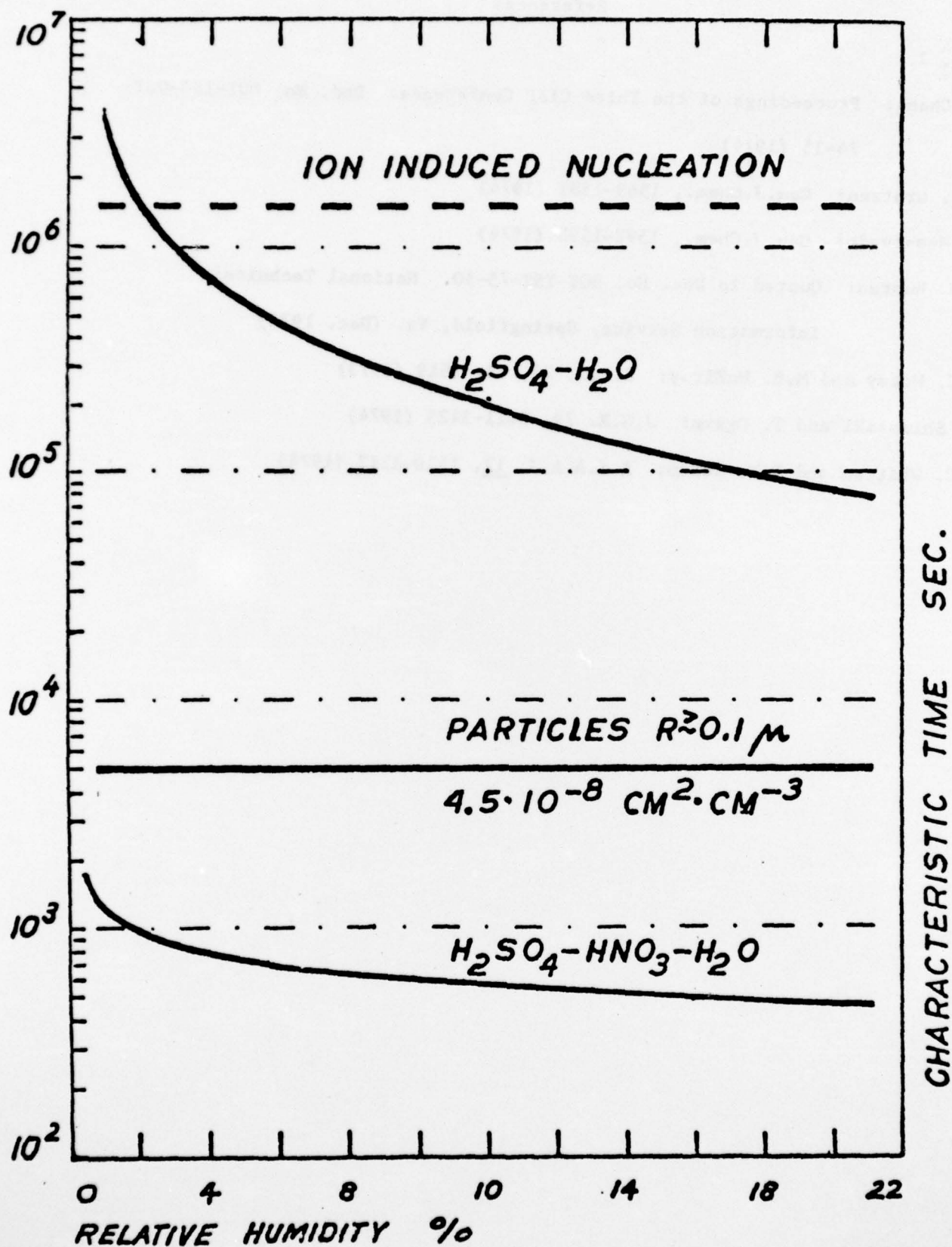E. Hesstvedt: Can.J.Chem., 1592-1598 (1974)

D.M. Hunten: Quoted in Doc. No. DOT-TST-75-50. National Technical Information Service, Springfield, Va. (Dec. 1974)

S.C. Wofsy and M.B. McElroy: J.G.R. 78, 15, 2619 (1973)

T. Shimazaki and T. Ogawa: J.G.R. 79, 3411-3423 (1974)

R.C. Whitten and R.P. Turco: A.I.A.A.J. 12, 1110-1117 (1974)

Figure 3

References

Fig. 3. Characteristic times for binary and ternary nucleation and for heterogeneous condensation on preexisting particles as function of relative humidity. (Temperature $-55^\circ C$, altitude $\lesssim 20km$)

Curve $H_2SO_4 - H_2O$:

Equilibrium water vapor pressure 3×10^{-2} Torr, actual water vapor partial pressure 3.5 ppmv.

Formation rate for H_2SO_4 from SO_2:

$$- \frac{d[SO_2]}{dt} = k \cdot [SO_2][OH][M] \rightarrow \frac{d[H_2SO_4]}{dt}$$

$[SO_2] \lesssim 0.2$ ppbv; $[OH] = 6 \times 10^5 cm^{-3}$; $k = 3 \times 10^{-31} cm^6 s^{-1}$; $[M] = 1.85 \times 10^{18} cm^{-3}$. Therefore, production rate for H_2SO_4: $c_B \approx 125$ molecules $\cdot cm^{-3}$.

Composition of stable embryonic droplet $\sim 80\%$ H_2SO_4, $\sim 20\%$ H_2O.

Critical size of stable embryo: 6-7 $\AA$. Vapor pressure of H_2SO_4 over pure solution 10^{-6} Torr. H_2SO_4 gas phase concentration required for the binary nucleation process to occur: $\sim 3.7 \times 10^8$ molecules $\cdot cm^{-3}$ (at 1% relative humidity, decreasing with increasing relative humidity).

For further details, see "The Interaction of Atmospheric Sulfur Compounds with Cloud and Precipitation Elements," Interim Report to NSF. ASRC Publ. No. 365, May 1975. Authors: G.K. Yue, C.S. Kiang, V.A. Mohnen and E. Danielsen.

$H_2SO_4-HNO_3-H_2O$:

All parameters the same as in the binary system. Critical composition of stable embryonic droplet: 75% H_2SO_4, 10% HNO_3, 20% H_2O.

Cont'd Fig. 3.

Under those conditions, the partial vapor pressure for this ternary system is estimated to be 10^{-13}, 10^{-9} and 10^{-7} Torr respectively. The minimum concentration of H_2SO_4 required for this ternary homogeneous nucleation process is of the order of 2×10^5 molecules·cm^{-3} (for 1% relative humidity). For further details see "The Interaction of Atmospheric Sulfur Compounds with Cloud and Precipitation Elements" cited above.

PARTICLES;

It is assumed that the preexisting "Junge layer" contains 0.3 µg/M^{-3} of particulate matter with an _average_ size of R ⩰ 0.1µ, a particle density of $\rho = 2$ g·cm^{-3} and a total number concentration of around 40. This leads to a total surface area per unit volume of A = 4.5×10^{-8} cm^2·cm^{-3}. Deposition of H_2SO_4 molecules on these preexisting particles ("condensation") is proportional to the surface area (this condition is fulfilled for all particles with R < 0.3µ). Sticking coefficient is assumed to be one. The characteristic time is then defined by

$$\tau_{particle} \approx \left(\frac{K\,T}{2\pi\cdot m} \right)^{-\frac{1}{2}} \times A^{-1}$$

K: Boltzman constant, T absolute temperature

m: mass of impinging gas molecule, here H_2SO_4

$A = \frac{3\cdot\chi}{R\cdot\rho} \times 10^{-6}$ cm^2·cm^{-3}

χ: particulate matter concentration in µg·m^{-3}

ρ: density in g·cm^{-3} and R: particle radius in microns

(Note that $\tau_{particle} \sim A^{-1}$, hence, a 10 fold decrease in specific surface area will result in a tenfold increase in characteristic time.)

(For further information, see above cited report.)

31

Cont'd Fig. 3.

Definition of characteristic time:

$$\tau_{nucleation} = \frac{\text{Minimum } H_2SO_4 \text{ concentration required for the homogeneous nucleation process}}{\text{Production rate of } H_2SO_4}$$
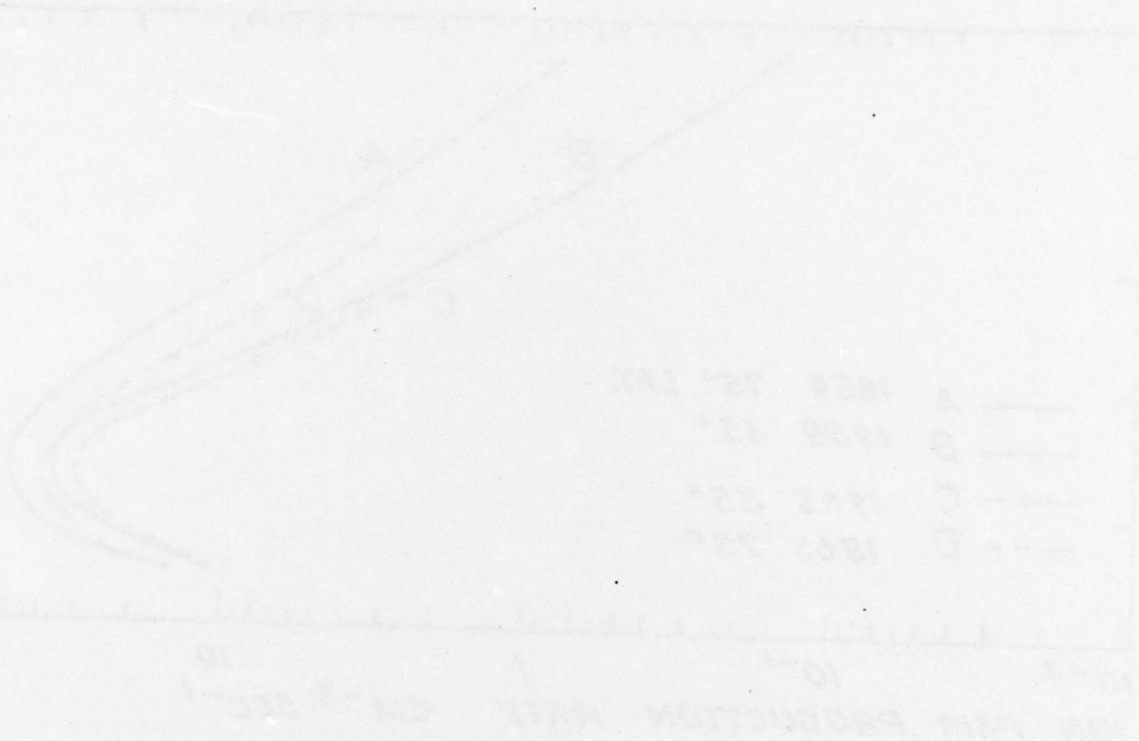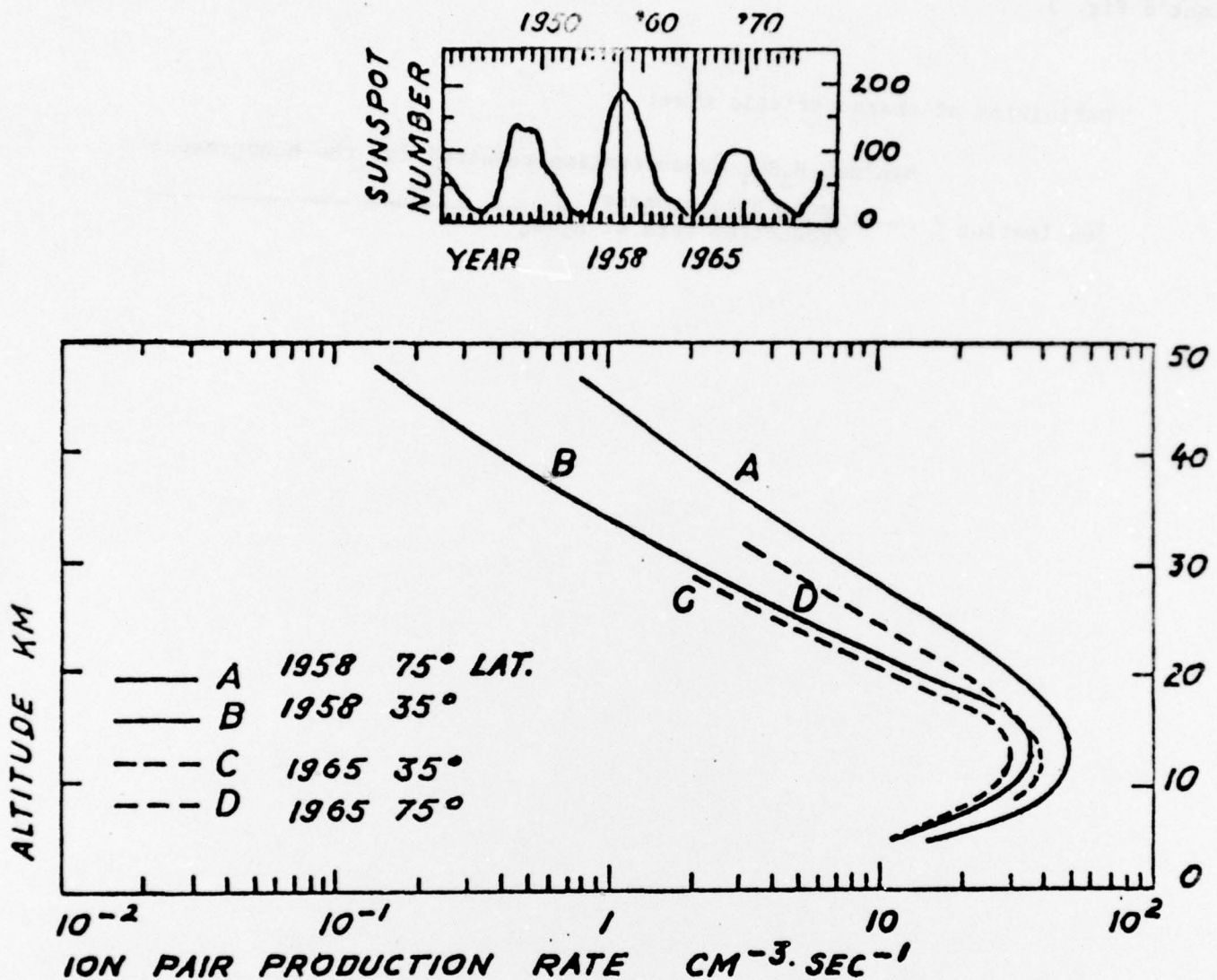
Figure 4

Source: H.V. Neher, J.G.R. 76, 1637-1651 (1971)

R.D. Hake, E.T. Pierce and W. Viezzee, "Stratospheric Electricity."
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M.A. Ruderman and J.W. Chamberlain, Doc.No. JSS-73-18-3, Institute
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Table 1

AVERAGE CONDITIONS IN STRATOSPHERE (20 km)

Trace Gas	Trace Gas Concentration in Molecules·cm^{-3}	Characteristic Ion[6] Interaction Time in Seconds	No.of Collisional Interactions During Average Lifetime of Ion[5]	
			For 1000 Ions/cm^3	For 5000 Ions/cm^3
O_2[1]	3.9×10^{17}	5×10^{-9}	2×10^{11}	4×10^{10}
CO_2[1]	5.9×10^{14}	2.9×10^{-6}	3.4×10^8	6.8×10^7
H_2O[1]	10^{13}	2×10^{-4}	5×10^6	10^5
O_3[1]	2.5×10^{12}	8×10^{-4}	1.3×10^6	2.6×10^5
NO_2[1]	1.5×10^9	0.75	1.3×10^3	2.6×10^2
NO[1]	5×10^8	4	250	50
HNO_3[1]	5×10^9	0.4	2.5×10^3	500
N_2O_5	4×10^6	500	2	–
NO_3	10^5	2×10^4	–	–
HCl[1]	2×10^9	1	1000	200
ClO	2×10^7	100	10	2
OH	6×10^5	3.3×10^3	(0.3)	–
O_2H	2×10^7	100	10	2
$O(^3P)$	3×10^5	6.7×10^3	(0.15)	–
CH_3O_2	1×10^7	200	5	1
Unknown:				
SO_2[2]	$<3.7 \times 10^8$	<5	<200	<40
H_2SO_4[3]	$>10^5$ but $<10^8$	<20	<50	<10
NH_3[4]	$<<3.10^9$	<<1	<<1000	<<200
Particles[7] (40 cm^{-3} R $\gtrsim$ 0.1μ)		2.5×10^3	–	–

Table 1

References

(1) Average of all measured values

(2) Based on 0.2 ppbv as assumed by Junge, C. E., Proceedings of the Int. Conf. on Structure, Composition and General Circulation of the Upper and Lower Atmosphere and Possible Anthropogenic Perturbation, Jan. 14-25, Melburne, Australia, Int. Union of Geodesy and Geophysics, Vol. 1, 85-97 (1974), Harrison and Larson (1974), Harker (1975) for model calculation

(3) Based on an average total sulfate content of 0.25 $\mu g/M^3$ (ambient) collected as aerosol

(4) Farmer, C. B., Can. J. Chem, 52, pp. 1544-1559 (1974).

(5) The lifetime of ions is defined by

$$\frac{dn^+}{dt} = - \alpha \cdot n^+ \cdot n^-$$

α: recombination coefficient, here assumed to be of the order of 10^{-6} $cm^3 \cdot sec^{-1}$

$$\tau_+ = \frac{1}{\alpha \cdot n}$$

n^+, n^- concentration of positive and negative ions per cm^3 respectively

τ_+ (1000 ions/cm^3) $\approx$ 1000 sec

τ_+ (5000 ions/cm^3) $\approx$ 200 sec

(6) Characteristic interaction time is defined by

$$\tau_c = \frac{1}{[\text{trace gas concentration}] \times \text{rate constant}}$$

A typical ion molecule rate constant of 5×10^{-10} $cm^3 \cdot sec$ is used. It is assumed that temporary or permanent attachment of the trace gas molecule to the ion occurs, or in some instances that an ion molecule reaction occurs. (See text)

(7) Ion annihilation time defined as (Zikmunda and Mohnen (1972)):

$$\tau = \frac{1}{\beta \cdot N}$$

β: attachment coefficient of ions to particles

$\beta = 10^{-5}$ cm^3 sec^{-1} for R $\approx$ 0.1μ

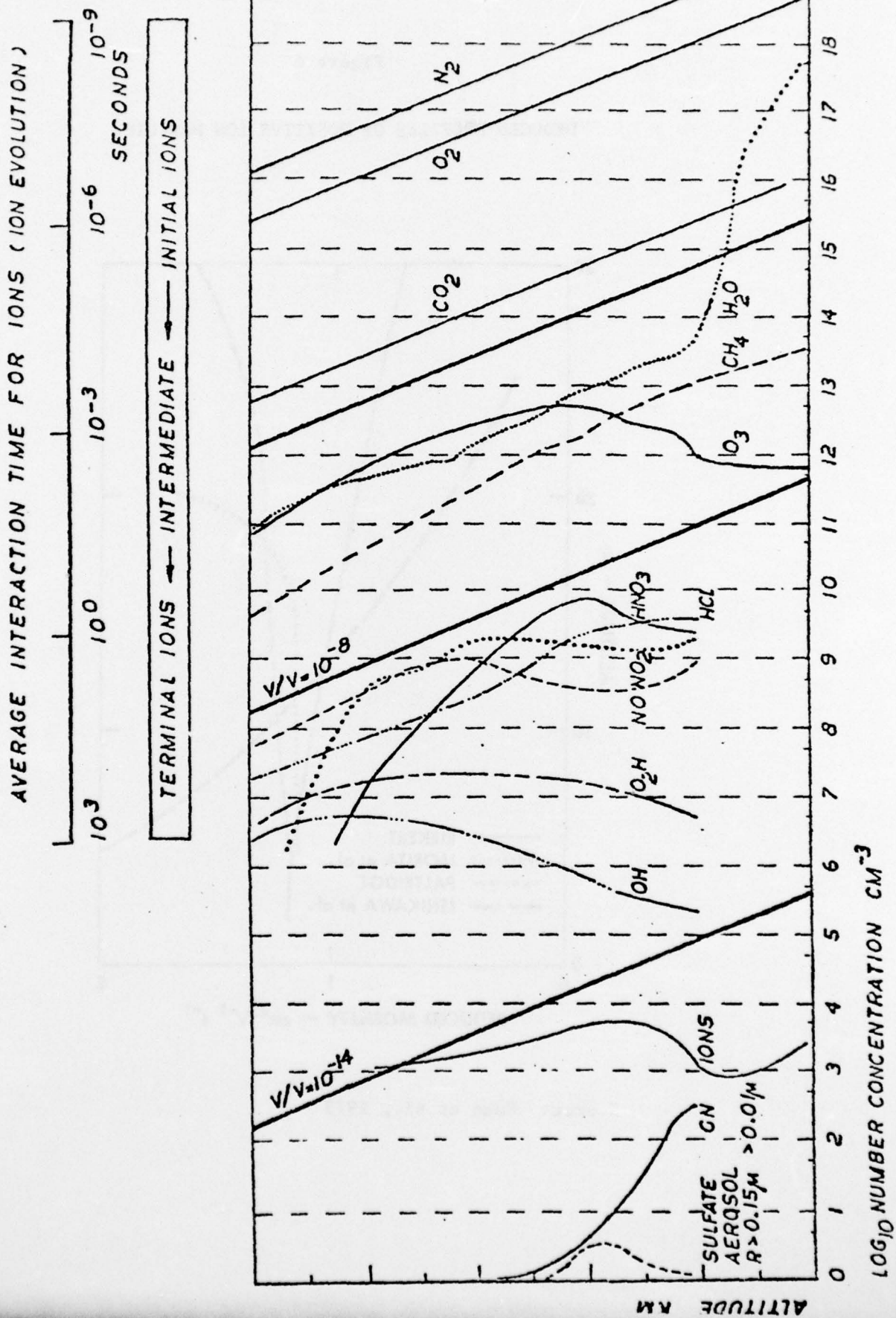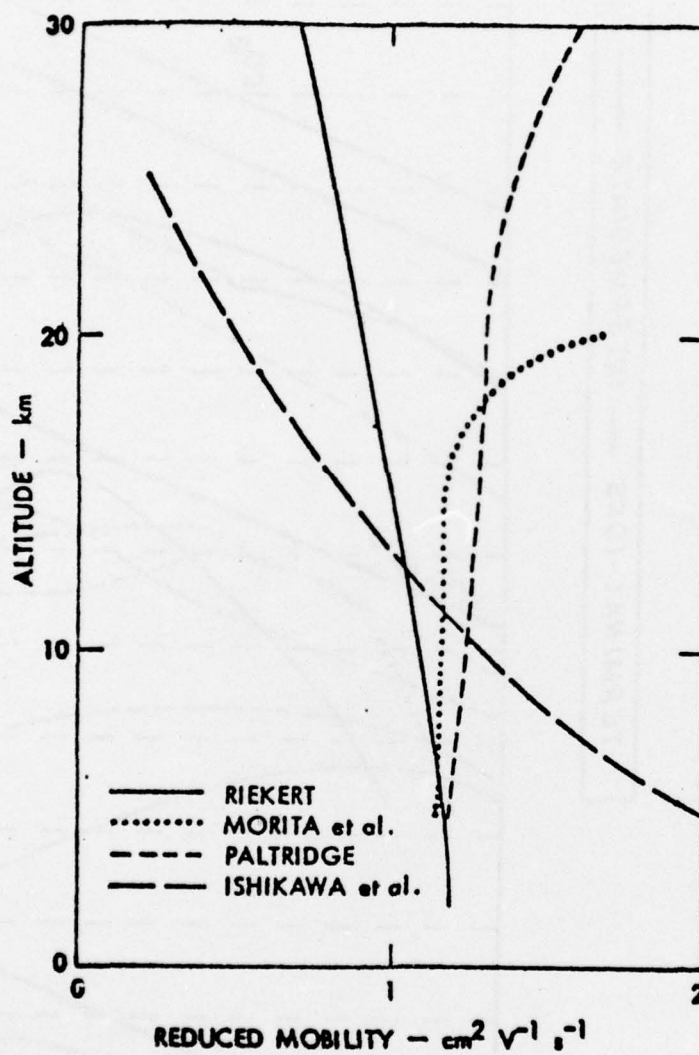N: total number of particles. N = 40 cm^{-3}

Figure 5

Figure 6

DEDUCED PROFILES OF POSITIVE ION MOBILITY

Source: Hake et al., 1973